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Improving precision and signal/noise ratios for MC-ICP-MS

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Abstract

High precision measurements of isotope ratios are improved by continuous innovations in multi-collector isotope ratio mass spectrometers. Recently, the Thermo Scientific TRITON *Plus* TIMS and NEPTUNE *Plus* MC-ICP-MS benefitted from the implementation of Faraday cup current amplifiers with 10^{13} ohm feedback resistors. This significantly improves the signal/noise ratio of ion beam measurements and the reproducibility of isotope ratios derived from low ion beam intensities (fA range). On the NEPTUNE *Plus*, these innovations follow the development of the Jet Interface option, itself enabling significant increases in ion beam intensities for both solution and laser ablation measurements. This paper presents data for uranium isotope ratios obtained with a NEPTUNE *Plus* equipped with both 10^{11} and 10^{13} ohm Faraday cup current amplifiers. The data presented here illustrate the benefits of such technology developments, which will have applications in the geosciences, environmental, nuclear and biomedical fields.

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1. Introduction

High-precision isotope ratio measurements are made possible by using mass spectrometers with arrays of collectors that can include ion counting devices in addition to Faraday cup detectors. The precision of ion counter and multi-ion-counter measurements is limited by inter-calibration, stability and linearity issues. However, they offer almost negligible baseline noise for the lowest absolute detection limits. Faraday cup detectors achieve the highest precision measurements using amplifiers that are highly stable and linear over a wide dynamic range of ion

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beam intensities. However, for samples where the total amount of analyte is limited, or where low-abundance isotopes are measured, the electronic baseline noise of the current amplifiers limits measurement precision.

Two approaches are possible to improve isotope ratio precisions and reproducibility from limited sample quantities or low-abundance isotopes: (1) improve ion beam intensities through more efficient sample utilisation with more efficient sample introduction into the ICP and ion sampling from the ICP; (2) improve the signal to noise (s/n) of measurements through improvements to the Faraday cup amplifier design.

In the following sections, we explore these innovations in multi-collector mass spectrometry using the latest generation of Thermo Scientific NEPTUNE *Plus* Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS).

2. Two major tools for refining isotope measurements

2.1. High performance ICP interface

Technical improvements increase the ion beam intensity, enabling improved analytical performances, providing access to isotope ratios of rare and precious materials.

The ion beam intensity is related to (1) the amount of material entering the ICP source; (2) the ionization efficiency; (3) and the efficiency of ion extraction. The first one is related to the efficiency with which a nebulizer produces 'useable' aerosol that can be injected into the ICP, as well as the concentration of the solution. The second one is a lesser issue, since the Ar plasma of an ICP source may virtually ionize all elements with 100% efficiency. The third is mainly related to the extraction and acceleration voltages and sample/skimmer cone geometries that sample ions from the ICP.

In 2009 Thermo Scientific launched the 'Jet Interface' option for NEPTUNE *Plus* MC-ICP-MS and ELEMENT 2 / XR SC-SF-ICP-MS instruments. This option includes an efficient Cetac Aridus II desolvating nebulizer system (Cetac, Omaha, USA), a high-performance interface pump that improves the vacuum at the interface and a new set of high-sensitivity cones (Jet sample and X type skimmer cones). It dramatically improves both the sample introduction to the ICP ion source and the sampling of ions from the ICP, resulting in improvements in trace elemental quantification and isotope ratio precision (for both solution and laser ablation mode).

2.2. 10^{13} Ω amplifiers

Another limitation to the precise and accurate measurement of isotope ratios is the low intensity of ion beams. This is of concern (1) for isotope systems with more than 2 orders of magnitude between the isotope abundances, and (2) for extremely low concentrations of the analyte in limited sample amounts. Such systems are historically measured with an array of ion counters, or a mixture of ion counters and Faraday cups. For small ion beams (less than about 200 fA (1.25 Mcps) the electronic baseline noise of the Faraday cup current amplifier significantly limits measurement precision.

In 2014 Thermo Scientific launched a new Faraday cup current amplifier with 10^{13} ohm feedback resistor (patent pending). Compared with standard 10^{11} Ω amplifiers, the 10^{13} Ω amplifier offers significantly improved s/n ratios for ion beams < 200 fA intensity[1,2] (equivalent to 20 mV on a standard 10^{11} Ω amplifier). The external reproducibility of isotope ratio measurements is correspondingly improved. The 10^{13} ohm amplifier can outcompete the SEM ion counter for beams as small as 20 kcps (ca. 2.7 fA, eq. to ~300 μV on a standard 10^{11} Ω amplifier). Thermo Scientific 10^{13} Ω amplifiers, are available for the NEPTUNE *Plus* (MC-ICP-MS), TRITON *Plus* (TIMS), HELIX MC and ARGUS VI (noble gas) instruments.

3. Analytical

The measurements presented here were performed in Bremen (Thermo Fisher Scientific, Germany), using a NEPTUNE *Plus* equipped with the optional Jet Interface and a variety of collectors, including Faraday cups with 10^{11} Ω amplifiers for ^{235}U and ^{238}U, high-gain amplifiers (10^{13} Ω) for ^{234}U and ion counter (SEM with RPQ energy filter) for ^{236}U. Uranium solutions were introduced using a Cetac Aridus II desolvating nebulizer system. The high-sensitivity Jet and X cones were used.

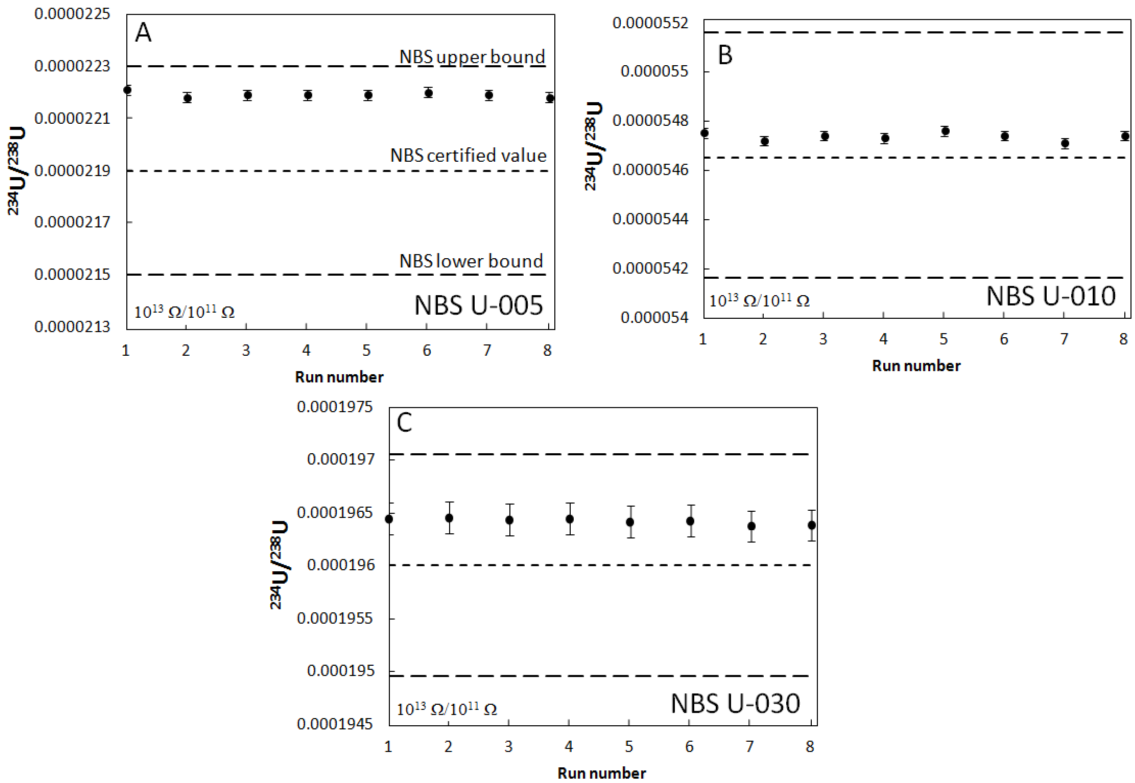

Fig. 1. Data obtained with the NEPTUNE *Plus* on NBS U certified reference materials.

4. Results

We focus here on the precise and accurate measurement of isotope ratios requiring high sensitivity and large dynamic range. As a consequence, we present U isotope ratios data obtained on Faraday cups, that would normally have been measured on ion counter(s).

4.1. NEPTUNE Plus U data

Figure 1 presents data obtained with the NBS U-0005, NBS U-010 and NBS U-030 standards with the Neptune *Plus*. In this example ^{234}U and ^{238}U were analyzed on faraday cups, with 10^{13} Ω and 10^{11} Ω amplifiers respectively. Sample consumption was ca. 20 ng total uranium per run, with a typical ion beam for the ^{234}U being of 8, 20 and 63 fA for 10 minutes acquisition (eq. to ca. 1, 2.5 and 7.9 mV on a 10^{11} Ω amplifier, respectively).

The relative standard deviation (RSD) on 8 repeated analyses is 0.44 ‰, 0.30 ‰ and 0.17 ‰, respectively. This level of precision was achieved with just one standardisation point and reflects the stability of the detector and mass bias during a period of 10.5 hours.

^{236}U was measured on an SEM with RPQ energy filter. For roughly equivalent ion beam intensities in NBS U-010, the ^{236}U precision was > 4 times poorer with the SEM-RPQ than the ^{234}U precision using 10^{13} ohm amplifier. The difference in precision is attributed to ion counter drift, correction of which would require additional standardization and therefore lower throughput of sample. However, since ^{236}U abundance can range from trace to absent, the lower detection limits of the SEM-RPQ detector is preferred for ^{236}U measurements. ^{234}U measurements are well suited to the 10^{13} Ω Faraday cup current amplifier since it is always present in uranium materials at trace levels.

Our data show exceptional combined mass bias and detector stability within a long sequence of measurements. Data obtained with the NEPTUNE *Plus*, with ca. 2.8 % of atoms from solution detected as ions, show that sample amounts as small as 0.4 pg ^{234}U yield ion beams of ca. 8 fA, enabling measurements of the $^{234}U/^{238}U$ isotope ratio with sub-‰ repeatability (2σ, n=10).

4.2. Discussion

MC-ICP-MS uranium isotope measurements are essentially a sample – standard comparison technique, where the external precision for the minor isotope abundances is limited by the low precision of the certified reference values. Sub-‰ measurement precision is readily achieved; however the absolute value is limited at the Sub-% level. For nuclear applications this is usually acceptable. The stability and dynamic range of the 10^{13} Ω Faraday cup current amplifier enables the gain to be precisely measured at the 0.1 ‰ (ε unit) level, such that these detectors can be used for higher precision analyses (see Sr and Nd data in References 1 and 2). The new amplifier technology is expected to have applications in the geosciences, environmental, nuclear and biomedical fields.

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